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Note: Available from the CIA Foreign Documents Branch is a complete translation of the Soviet article discussed below: Catalytic Hydrocondensation of Carbon Monoxide with Olefins. I Hydrocondensation of CO with Ethylene; Ya T. Eidus, ND Zelinskii and KV Puzitskii - Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, 1949, 110-14.

Summary of Paper

1. Previous conclusions that methylene radicals are important intermediates in both decomposition and synthesis reactions are reviewed. Mixtures of carbon monoxide plus hydrogen, with and without ethylene, were reacted over 25 ml of catalyst at atmospheric pressure, 190-200°C., near 100 space velocity. Clear evidence that ethylene is converted, mainly to liquid products, is presented. A possible reaction mechanism involving methylene radicals is offered.

General Evaluation

2. The experimental work involved is of good quality and the experimental data are carefully presented, within the omissions discussed later. The presentation is somewhat rough and preparation of the paper seems hurried. Readers gain the impression that the data are used to promote theories which are then used to support the data. The novelty of the work seems overly stressed.

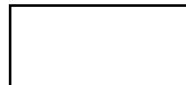
Comparison With US Work

3. Related work has been done in the USA and elsewhere. Ethylene has been added in small quantities to hydrogen plus CO, and hydrogen plus CO have been added to ethylene. Although participation of ethylene in the reaction has been recognized, the design of the US experiments was not as well suited to observing the prominent reaction reported here. The US results would hardly warrant classification of the ethylene conversion as a new reaction.

Competence of Work

4. Zelinskii has nearly 50 years of world-renowned research on hydrocarbons behind him. Eidus has been known for nearly 10 years. Puzitskii presumably did the experimental work. Both work and presentation should be expected to rank high. To the informed worker in the field, the experimentation is about par, but presentation is disappointing, for the reasons outlined below.

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5. Such a paper could not be published as such in a US journal of the caliber of Bull. Acad. Sci. USSR for the following reasons:

- a. All reference to the catalyst used is carefully avoided.
- b. Previous non-Russian literature is disregarded.
- c. Feed and product gas compositions are unnecessarily detailed.
- d. Two important statements are entirely unsupported:
 - 1) The principal product consists of aliphatic hydrocarbons.
 - 2) Propyl alcohol was identified.
- e. The theoretical or mechanism section could be presented more convincingly.

Other Comments

- 6. The balance between the various parts of the paper is interesting. Where numbers are available, they are presented in great detail. Where no numbers are available, the presentation is extremely brief. Whether the data are numerically supported or not is ignored in discussion of significance. Presumably additional numbers are available, but are withheld from publication.
- 7. The experimental work was purportedly done before the authors learned of the German Oxo reaction. They should have learned of this reaction not later than January 1946. The paper was submitted in March 1948, and published early in 1949. This schedule belies the impression that the paper was prepared rather hurriedly for the purpose of establishing the priority of the authors in discovering this reaction.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE
WITH OLEFINS. I. HYDROCONDENSATION OF CARBON
MONOXIDE WITH ETHYLENE.

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IZVESTIYA AKADEMII NAUK SSSR, OTDELENIE
KHIMICHESKIKH NAUK (Bull. Acad. Sci.
USSR, Dept. Chem. Sci.)
1949, 110 - 14

This is a complete translation of the original article.

ABSTRACT

A new reaction, i.e., catalytic hydrocondensation of carbon monoxide with ethylene under atmospheric pressure, was investigated. The principal product consists of aliphatic hydrocarbons. In the formation of liquid and solid products, one volume carbon monoxide reacts with 2 - 3 volumes hydrogen and 3 - 4.5 volumes ethylene. In experiments with a gaseous feed made up of $1\text{CO} : 2\text{H}_2 : 3\text{C}_2\text{H}_4$, about 80% ethylene was found to go to the condensed phase and only about 20% was hydrogenated to ethane.

The mechanism of formation of hydrocarbons is discussed in the light of the multiplet theory and the principle of preservation of the valence angles in catalysis.

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N. D. Zelinskiĭ called attention to reactions in which a material part is played by methylene radicals on the surface of the catalyst. As early as 1934 N. D. Zelinskiĭ and N. I. Shuĭkin (1) observed partial decomposition of cyclohexane in the presence of hydrogen on nickel carried on alumina, forming methylene radicals and methane. Among the reaction products methyl- and dimethylcyclohexane, as well as toluene and xylene, were found. Formation of these products was explained by the fact that methylene radicals resulted from decomposition of cyclohexane and methylated cyclohexane. In 1940 Ya. T. Eidus and N. D. Zelinskiĭ (2) experimentally confirmed for the first time the hypothesis pertaining to intermediate formation of methylene radicals in catalytic synthesis of higher hydrocarbons from carbon monoxide and hydrogen (3). Polymerization of methylene radicals received little study heretofore. It follows from the experiments reported by A. M. Butlerov (4) that nascent methylene groups can couple to ethylene. It could be assumed that ethylene is also a primary intermediate compound of linear polymerization of methylenes on the surface of the catalyst. This prompted the present authors to study the possibility of condensing ethylene with

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carbon monoxide in the presence of hydrogen. The first results of this investigation are reported below.

EXPERIMENTAL PART

The reaction vessel consisted of a glass tube 10 mm. in diameter, in which the catalyst formed a layer 35 - 40 mm. long. Automatic regulation of the furnace temperature within $\pm 1.5^\circ$ was provided for. Carbon monoxide and hydrogen, purified in the conventional manner, were used to make up the feed gas, usually in the ratio of 1 : 2. The content of ethylene did not exceed 50%. It was prepared by dehydration of ethanol over alumina, was purified by passing it through concentrated sulfuric acid, a solution of caustic alkali and a tube with solid caustic potash and activated carbon. The initial gaseous mixture was passed at an approximate hourly space velocity of 100. The experiments were performed at 190 - 200° and atmospheric pressure in a flow system apparatus and were interrupted for the night. The reaction products were collected in two receivers; in the first, kept at room temperature, an aqueous and a supernatant oily layer ("heavy oil") were collected, and in the second "light oil" was condensed at -80°.

Table 1 shows the results obtained over different samples of the catalyst of the same composition, using gaseous mixtures containing 0.33 and 50% ethylene. The yields were calculated on the total amounts of gases charged. As seen from these data, a 50% content of ethylene results in an average yield of oil, reaching 343.3 ml./cu. m., or 29.6 ml./l./hr.

Table 2 shows results of experiments in which a mixture of 100 : 2H₂ : 3C₂H₄ was used in the presence of a particularly active catalyst. The yield of oil within 49 hours of the working period amounted to 333 - 465 ml./cu. m. or 33 - 49 ml./l./hr. at a space velocity of 114 - 135. The highest yield was 465.2 ml./cu.m. or 49.2 ml./l./hr. at a space velocity of 118. The yield of reaction water was 55 - 96 ml./cu. m. The ratio of the volumes of the light and heavy oils was not constant and, in the course of the process, decreased from 1.42 to 0.85. In each experiment referred to in Table 2 the initial and off gas (emitted from the second receiver) were analyzed. The gas analysis was done in the conventional way, using the Hempel apparatus. Ethylene was determined with bromine water, carbon monoxide with ammoniacal cuprous chloride, hydrogen by combustion with air over platinized asbestos, saturated hydrocarbons by combustion with oxygen in a pipette according to Winkler-Dennis.

The composition of the gases charged and emitted in the experiments shown in Table 2 is described by the analytical data reported in Table 3. The last-mentioned Table served as the basis for the calculation of the extent to which each component of the gaseous mixture participated in the reaction.

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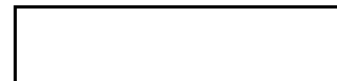


TABLE 1

Duration, Hours	Initial Gas Mixture	Space Veloc- ity	Average Yield, ml. per cu. m.				Average Yield of the Total Oil, ml. per l. per hr.
			Heavy Oil	Light Oil	Total Oil	Reaction Water	
90	$100:2H_2:3C_2H_4$	93	130.8	212.5	343.3	29.6	30.2
71	$100:2H_2:1.5C_2H_4$	106	107.5	88.1	195.6	19.4	85.1
68	$100:2H_2$	83	76.2	46.6	122.8	9.0	178.7

TABLE 2

Experiment No.	Duration, Hours	Space Veloc- ity	Per Cent Contrac- tion	Average Yield, ml. per cu. m.				Average Yield of the Total Oil, ml. per l. per hr.
				Heavy Oil	Light Oil	Total Oil	Reaction Water	
1	7	135	72	159.8	228.4	388.2	54.8	46.5
2	7	118	67	207.0	258.5	465.5	77.6	49.2
3	7	119	64.5	202.9	217.8	420.7	95.6	43.2
4	7	122	63	191.2	170.5	361.7	87.8	38.3
5	7	115	63.5	234.1	152.5	386.6	81.7	38.9
6	7	114	55	196.4	136.4	332.8	87.3	33.4
7	7	120	46	188.8	161.8	350.6	64.7	35.6

TABLE 3

Experiment No.	Composition of the Feed Gas							
	Liters				Per Cent by Volume			
	CO	H ₂	C ₂ H ₄	N ₂	CO	H ₂	C ₂ H ₄	N ₂
1	3.88	7.44	10.57	2.45	15.7	30.1	42.8	9.9
2	3.25	6.36	9.72	2.11	15.1	29.6	45.2	9.8
3	2.95	6.49	9.38	2.56	13.6	29.9	43.2	11.8
4	3.57	6.80	8.99	2.59	16.0	30.5	40.3	11.6
5	3.71	6.16	8.50	2.53	17.6	29.2	40.3	12.0
6	4.01	6.39	7.93	2.63	19.2	30.6	38.0	12.6

TABLE 3 (Cont'd.)

Experiment No.	Composition of the Off Gas									
	Liters					Per Cent by Volume				
	CO	H ₂	C ₂ H ₄	C ₂ H ₆	N ₂	CO	H ₂	C ₂ H ₄	C ₂ H ₆	N ₂
1	1.11	0.94	0.73	1.47	2.43	16.0	13.7	10.6	21.3	35.2*
2	1.60	0.67	0.90	1.89	2.01	22.5	9.4	12.7	26.6	28.4*
3	1.54	0.48	1.39	1.68	2.52	20.0	6.2	18.0	21.8	32.7*
4	1.83	0.84	1.42	1.54	2.58	22.3	10.2	17.3	18.8	31.4
5	1.88	0.41	1.19	1.64	2.56	24.4	5.3	15.5	21.3	33.3
6	2.71	1.37	1.62	1.22	2.60	28.8	14.6	17.2	13.0	27.7

* In the experiments 1, 2 and 3 the emitted gas contained 3.1, 0.8 and 1.1 per cent CO₂, respectively.

The number of liters of each component participating in the reaction is shown in Table 4, where the percentage of the reacting component on its amount in the initial mixture is also recorded. Further, the number of liters of ethane formed and its percentage on the hydrogen and ethylene reacted are also given. By subtracting this number from 100, the percentage of hydrogen or ethylene consumed in the formation of the condensed phase is obtained.

It follows from Table 4 that ethylene reacts to the extent of 80 - 93% and that only 15 - 22% of the ethylene reacted is consumed in the formation of ethane. Hydrogen reacts to the extent of 87 - 99%. Ethane formation consumes 20 - 33% of the hydrogen reacted. The conversion of carbon monoxide amounts first to 71.4%; subsequently, the percentage of carbon monoxide reacted is stabilized at 48 - 51%. In the Experiment 6, it dropped to 32.4%; however, this drop is to be explained, as is shown below, not by the relative decrease of the extent of participation of carbon monoxide in the reaction, but by a certain absolute increase of its content in the initial gaseous mixture.

Table 5 reports the number of liters of the individual reacting components consumed in the formation of liquid and solid products, as well as their ratio. These data for hydrogen and ethylene were obtained by subtracting from the total number of liters of reacted hydrogen or ethylene, as shown in Table 4, the number of liters of ethane formed, which is also reported there. The ratios were obtained by dividing the number of liters of hydrogen or ethylene shown in Table 5 by the number of liters of reacted carbon monoxide. It is seen from Table 5 that 2 - 3 volumes hydrogen and 3 - 4.5 volumes ethylene react per each volume carbon monoxide when liquid and solid products are formed.

The yields of oil from a mixture of $1\text{CO} : 2\text{H}_2 : 3\text{C}_2\text{H}_4$ is shown by the Tables 1 to 5 to reach 300 to 400 ml./cu. m., or 30 - 40 ml./l./hr., and ethylene actively participates in this process.

A new reaction of hydro-condensation of carbon monoxide with ethylene (5) is revealed by these data; about 80% of ethylene reacts in the formation of the condensate and only about 20% of it is hydrogenated to ethane.

A preliminary investigation of the reaction products, oil as well as the reaction water, indicated an insignificant amount of oxygen-containing compounds, particularly alcohols, to be present in them. Propyl alcohol was identified. The principal amount of the product is a mixture of saturated and unsaturated aliphatic hydrocarbons. A more detailed investigation will constitute the subject of a subsequent paper.

The formation of hydrocarbons in hydrocondensation of carbon monoxide with

TABLE 4

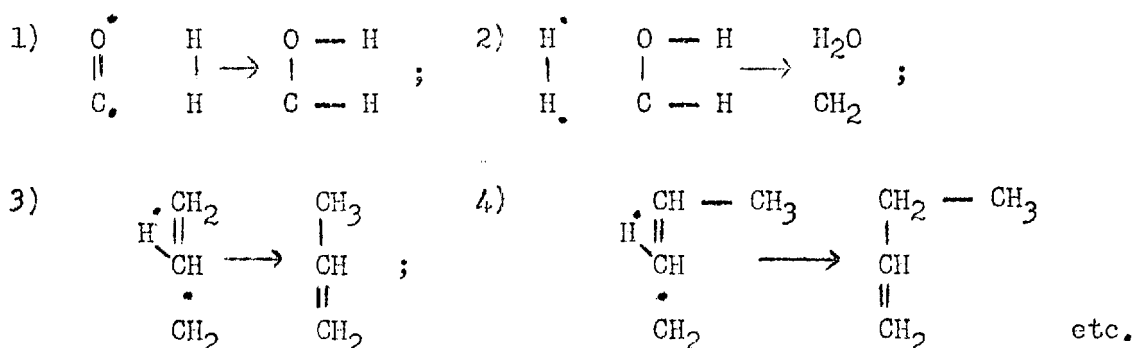
Experiment No.	Reacted						Ethane Formed		
	Liters			Per Cent on the Initial Component			Liters	Per Cent on Hydrogen Reacted	Per Cent on Ethylene Reacted
	CO	H ₂	C ₂ H ₄	CO	H ₂	C ₂ H ₄			
1	2.77	6.50	9.84	71.4	87.4	93.1	1.47	22.6	15.0
2	1.65	5.69	8.82	50.8	89.4	90.8	1.89	33.2	21.4
3	1.41	6.01	7.99	47.8	92.6	85.2	1.68	27.9	21.0
4	1.74	5.96	7.57	48.7	87.6	84.2	1.54	25.8	20.3
5	1.83	5.75	7.31	49.3	93.3	86.0	1.64	28.5	22.4
6	1.30	5.02	6.31	32.4	93.9	79.5	1.22	24.8	19.3

TABLE 5

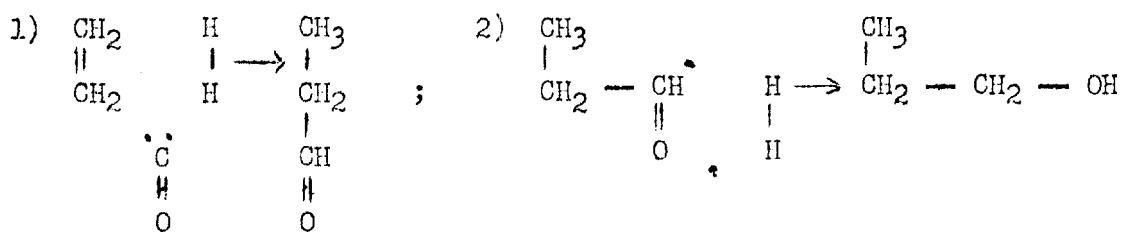
Experiment No.	Liters CO	Liters H ₂	Liters C ₂ H ₄	CO : H ₂ : C ₂ H ₄
1	2.77	5.03	7.37	1 : 1.8 : 2.7
2	1.65	3.80	6.93	1 : 2.3 : 4.2
3	1.41	4.33	6.31	1 : 3.1 : 4.5
4	1.74	4.42	6.03	1 : 2.5 : 3.5
5	1.83	4.11	5.67	1 : 2.2 : 3.1
6	1.30	3.80	5.09	1 : 2.9 : 3.9

ethylene occurs apparently in accordance with the principle of preservation of the valence angle in catalysis (6), through polymerization of methylene radicals involving participation of ethylene in this reaction. The mechanism of formation of methylene groups proposed by one of the present authors (7) makes it possible to express this process by the multiplet scheme, as shown below.

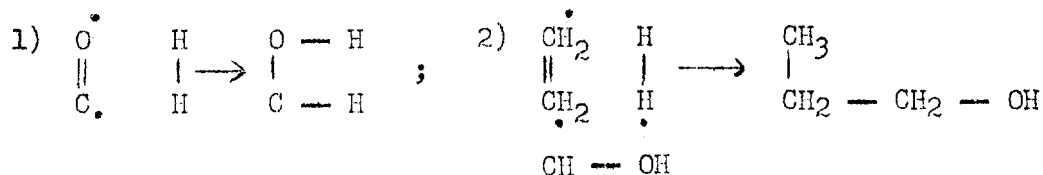
I



IIa



IIb



The formation of propyl alcohol may occur according to the mechanism IIa or IIb. In the former, the intermediate compound is acetaldehyde. The scheme I shows doublet reactions and involves a change in the valence of the carbon atoms. In schemes II and IIb doublet as well as triplet reactions occur, the latter also involving a change of valence. These reactions offer a rare example of the applicability of Balandin's multiplet theory (8) to processes occurring with change of the valence of the reacting atom.

The principal results of this work were obtained before information pertaining to the "OXO" synthesis became available to the authors. An essential difference should be noted between this process, occurring under elevated pressure and leading to formation of aldehydes, and the hydrocondensation of carbon monoxide with ethylene, which occurs under atmospheric pressure, forming hydrocarbons.

Received March 12, 1948.

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